NEW APPLICATIONS OF SUBSTITUTED 1,10-PHENANTHROLINE DERIVATIVES IN ANALYTICAL CHEMISTRY

BY

WALLACE HUTCHINSON McCURDY, JR.

B.S., Pennsylvania State College, 1947
M.S., University of Illinois, 1948

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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NEW APPLICATIONS OF SUBSTITUTED 1,10-PHENANTHROLINE DERIVATIVES IN ANALYTICAL CHEMISTRY

Over the past fifteen years the number of published papers concerning 1,10-phenanthroline and its substituted derivatives has been steadily increasing. The ability of these reagents to form coordination complexes with most of the transition metal ions has been well established.

However, only the iron 1,10-phenanthroline complexes have thus far found a significant place in analytical chemistry. Copper, molybdenum, cobalt, ruthenium, chromium, palladium and others in addition to iron yield colored complexes with 1,10-phenanthroline of slight analytical value. Studies of these elements with various substituted 1,10-phenanthrolines may uncover valuable applications for these complexes in gravimetric, volumetric and spectrophotometric methods of analysis.

The present work was undertaken to investigate 1,10-phenanthroline and substituted derivatives as analytical reagents for copper. Results of accurate quantitative determinations of small amounts of copper are reported using a new copper specific. During this research several new sensitive reagents for iron were discovered and these will be described briefly. It is hoped that this writing will serve to stimulate such studies with other metal ions.

PART I

SPECTROPHOTOMETRIC STUDIES OF CUPROUS 1,10-PHENANTHROLINE COMPLEXES

Tartarini (1) reported the isolation of mono and bis 1,10-phenanthroline cuprous salts that yield intense red-

orange colored solutions in ethyl alcohol. The analytical applicability of this color according to a procedure developed by Moss and Mellon (2) has been limited by the apparent instability and unextractibility of the complex and by interference with iron which is commonly present.

The spectrophotometric study of a large group of substituted 1,10-phenanthroline cuprous complexes was undertaken (1st) to test the predictable effect of the positions of substitution in 1,10-phenanthroline on the absorption spectra, (2nd) to discover superior spectrophotometric reagents for copper to those now available and (3rd) to evaluate several physico-chemical variables in order that the synthesis of a superlative 1,10-phenanthroline copper complexing agent might be suggested.

The following 1,10-phenanthroline derivatives used in this investigation were obtained through the cooperation of Dr. F. H. Case of Temple University (3).

1,10-PHENANTHROLINE COMPOUNDS

3-; 4-; 5-methyl
2,9-; 3,4-; 3,5-; 3,6-; 3,7-; 3,8-; 4,5-; 4,6-; 4,7-; 5,6-dimethyl
3,4,6-; 3,4,7-; 3,4,8-; 3,5,6-; 3,5,7-; 3,5,8-; 3,6,7-; 4,6,7-trimethyl
2,4,7,9-; 3,4,6,7-; 3,4,6,8-; 3,4,7,8-; 3,5,6,8-tetramethyl

4-; 5-phenyl
4,6-; 4,7-diphenyl

At the very outset, it was discovered that the cuprous 1,10-phenanthroline complexes may be extracted from neutral or slightly alkaline solution with n-amyl, isoamyl or n-hexyl alcohol. Because the nitro and halogen substituted derivatives form unstable complexes which are only slightly extractible, they were not included in this study.

Observation of the pH of maximum color extraction for cuprous complexes of the compounds listed above showed that

the 2,9 positions of substitution cause extraction to occur from acid solution (pH-3), the 4,7 positions permit complete extraction only from basic solution (pH-9) while the 3,8 or 5,6 positions allow extraction to take place at nearly the same pH as the 1,10-phenanthroline cuprous complex (pH-7). The large stability of the complexes containing 2,9-positioned methyl substitutions has been attributed to favorable structure-size relationships.

Fading of isoamyl alcohol solutions of the cuprous complexes of 1,10-phenanthroline derivatives other than the 2,9-dimethyl compounds was found to involve both pH and air oxidation effects. A procedure was developed which largely removes this difficulty.

Formulae of the two 1,10-phenanthroline complexes with copper(I) previously reported (1) were confirmed. Although only the bis complex was detected by the method of continuous variations, a mono 1,10-phenanthroline cuprous salt was precipitated from strong acid solution.

The visible absorption spectra of 25 methyl substituted bis 1,10-phenanthroline copper(I) complexes were examined. The predictability of the wave length of maximum absorption observed with the ferrous complexes (4) has been extended to the cuprous complexes. Calculated and experimental wave lengths agree within $\pm$ 1.0 mu. A similar relationship was detected for the wave lengths of maximum absorption of the phenyl substituted complexes studied.

As was also shown to be the case with the ferrous complexes (4), substitution in the 4 or 7 positions yields a marked increase in the molecular extinction coefficient of the cuprous complex obtained. The highest value was calculated for the 4,7-diphenyl-1,10-phenanthroline complex (12,140).

A study was made of the effects of pH on the ultra violet spectra of several 1,10-phenanthroline bases and their cuprous complexes. A marked increase in the intensity of absorption in the 2000 to 2300 A° region occurs upon raising the pH or

addition of cuprous ion. This has been ascribed to changes in electronic resonance of the nitrogen atoms and associated chromophoric groups which take place upon formation of the free base or metal complex ion.

PART II

COPPER SPECIFIC REAGENTS

The description of the $CH_3-C=N-C-C-N=C-CH_3$ copper specific functional group by Hoste (5) suggested the investigation of 2,9-dimethyl-1,10-phenanthroline derivatives as superior copper specific chelating compounds. The 2,9-dimethyl and 2,4,7,9-tetramethyl-1,10-phenanthroline compounds were found to be completely specific for cuprous copper under the conditions specified for the reaction.

Extinction coefficients determined for these complexes at 455 and 451 mu wave lengths are 7950 and 8860 respectively. Both compounds permit extraction of copper by n-amyl, isoamyl or n-hexyl alcohol over a pH range of 3 to 10. The absorption complies with Beer's law and remains essentially unchanged for at least 10 days standing in each case.

The limits of qualitative identification are 0.03 gammas and 0.009 gammas for the dimethyl and tetramethyl substituted copper specifics.

Quantitative data are presented for the determination of 1 to 2 ppm of copper in the presence of 1 to 2 gms. of iron using citrate masking agent.

Partial recovery of the complexed reagent from alkaline copper cyanide solutions has been achieved employing benzene extraction. The 2,9-dimethyl-1,10-phenanthroline has now been given the trivial name "Neo-Cuproine" by analogy to the term "Cuproine" assigned to 2,2′-diquinoline by Hoste (5).

PART III

EXTREMELY SENSITIVE REAGENTS FOR IRON AND COPPER

During the course of this research, several compounds were discovered which double the sensitivity obtained with the 1,10-phenanthroline tests for iron and copper.

Quantitative determinations of copper were carried out using 4,7-diphenyl-1,10-phenanthroline. While the reagent is very sensitive for traces of copper(I), the color stability in isoamyl alcohol is poor. It is believed that the addition of methyl groups to the 2,9 positions of this compound will produce a spectrophotometric copper specific reagent superior to any now known. The properties of this complex have been predicted.

The most sensitive reagents for iron yet discovered are reported here. Both 4,7-dinovalamine and 4,7-diphenyl-1,10-phenanthroline form ferrous complexes with very high molecular extinction coefficients (19,000 and 22,400). The sensitivity of these reagents is further enhanced by the favorable solubility of the ferrous complexes in isoamyl or n-hexyl alcohol. Although the 4,7-dinovalamine-1,10-phenanthroline ferrous complex must be extracted from ammoniacal solution, the corresponding 4,7-diphenyl complex is removed quantitatively from solution even at pH-2.

Qualitative sensitivity limits of .008 and .001 gammas of iron have been established for the 4,7-dinovalamine and 4,7-diphenyl-1,10-phenanthroline reagents. Beer's law was found to be valid for the 0.2 to 10 ppm range of concentrations studied. The color stability of these alcohol solutions is very good.

The red and green forms of the 4,7-dinovalamine-1,10-phenanthroline ferrous complexes at pH-7.0 and 2.0 respectively were shown to be tris complexes by the method of continuous variations. The exact reason for the color change

is unknown but it may be assumed that the large amino groups cause the ferrous complex to act as an acid-base indicator.

A number of proposals are made for future investigations employing these reagents.

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VITA

Wallace Hutchinson McCurdy, Jr. was born on November 16, 1926 in Pittsburgh, Pennsylvania and received his elementary education there. After graduating from Crafton High School in 1944, he enrolled in the war acceleration education program at the Pennsylvania State College and received the degree of Bachelor of Science in Chemistry from that institution in June, 1947.

He entered the Graduate College of the University of Illinois in September of that year. In August, 1948 he received the degree of Master of Science from this university. He held a graduate half-time teaching assistantship from September, 1947 to June, 1950, and a University Fellowship from September, 1950 to February, 1951.

He is a member of the following honoraries and professional societies: Phi Lambda Upsilon, Sigma Xi and the American Chemical Society.